Modified Stranski-Krastanow mode for Ge island growth on (001) Si at high temperatures

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Transmission electron microscopy is used to study the morphology and the composition profile of "pure" Ge islands grown at high temperature on (001) Si by molecular beam epitaxy. An alloying process, involving mass transport from the substrate to the islands during the island growth, was identified. It was found that, as a result of Si mass transport to the Ge islands, the island/substrate interface moves towards the substrate, and trenches form on the substrate surface around the islands. Reduction of the misfit strain at the island/substrate interface is the driving force for this process.

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Semiconductor quantum dots (QDs) are attracting increasing interest because of their significant opto-electronic properties. [1] Although QDs can be produced in many ways, the method of coherent island formation is of great importance for materials with large lattice mismatch (such as Ge(Si)/Si [2,3] and $In_xGa_{1-x}As/GaAs$ [4]) because of the possible combination of the QD growth and semiconductor integration techniques. Of crucial importance in determining the opto-electronic properties of the QDs are the structural parameters of the QDs including the shape, size and composition. [5] Uniformity in and control over these parameters are a prerequisite for many applications. To achieve this goal, a complete understanding of the mechanism of the QD growth is necessary. Although many investigations have concentrated on the shape and the size [6,7] and on the evolution [8,9,10] during the QD growth, relative little attention has been paid to the composition. [11,12,13]

In the classical Stranski-Krastanow [14] (S-K) mode of coherent island formation, one material with a different lattice parameter and low interfacial energy is initially deposited on a substrate surface, layer by layer, forming a "wetting layer". When the wetting layer reaches a critical thickness (usually three to five monolayers for pure Ge on Si (001) [3,15]), island growth starts to partially release the mismatch strain energy between the epitaxial layer and the substrate. However, in the case of InAs/GaAs, recent investigations suggest that, for higher temperature growths, there is significant mass transport from both the wetting layer and the substrate to the islands. [16] This suggests that the classic S-K growth mechanism needs to be modified to explain the complicated island growth phenomenon. In this Letter, we demonstrate evidence for mass transport from the Si substrate to the Ge islands during high temperature molecular beam epitaxy (MBE) growth of "pure" Ge islands on the (001) Si substrate. The mass transport changes the composition of the islands, moves the Ge/Si interface below the original substrate surface, and forms a trench around each island. It is proposed that the driving force for this mechanism is a reduction in the strain energy. As a consequence, a modified S-K mode is suggested for the island growth at high temperature.

P-type (001) Si wafers with resistivity of 1 Ω cm were used as substrates. Ge islands were grown on the Si substrates by solid source MBE at a growth temperature of 700°C and a growth rate of 0.02 nm/s. Prior to Ge deposition, a 30 nm thick Si buffer layer was grown on the substrates. Two different thicknesses of Ge were then deposited: A (0.8 nm) and B (1.4 nm).

Plan-view transmission electron microscopy (TEM) specimens were prepared using chemical etching with a solution of HF and HNO_3 in the ratio of 1:9. Cross-section TEM specimens were prepared using Ar^+ ion-beam thinning in a Gatan PIPS with an accelerating energy of 3 keV. TEM investigations were carried out using a Philips CM12 TEM operating at 120 keV, a Philips EM430 operating at 300 keV and a Philips CM120 BioTEM equipped with energy filtered imaging operating at 117 keV.

Figures 1 (a) and (b) show two typical [001] zone-axis bright-field diffraction contrast images taken from samples A and B respectively. It was found that most of the islands in sample A are uniform in size with a base diameter of approximately 95 nm. However, islands in the sample B have a range of sizes, with the smallest being of a similar size to those in the sample A. The reason for the size non-uniformity in strained island growth has been reported in the literature. [9,10,17] It was also found that small islands in both samples have a square shaped base with rounded corners, as has been observed by atomic force microscopy (AFM).[18]

Cross-section TEM studies showed that, along <110>, islands in both samples have similar height to base-diameter aspect ratios (about 1:5), irrespective of the size of the island. Figures 2 (a) and (b) are typical bright-field cross-sectional TEM images of the islands in the two samples. Figure 2 (c) is an enlarged image of a part of Fig. 2 (a), clearly showing a thin wetting layer on the Si substrate uniformly across the entire interface and a trench by the edge of a coherent island. Figure 2 (d) is an enlarged image of a part of Fig. 2 (b), showing similar trench feature as Fig. 2 (c) at an area surrounding the edge of a relaxed island. Extensive TEM investigations on the cross section specimens show that: (i) the islands in sample A and the smaller islands in sample B are coherent, while the larger islands in B are multi-faceted and relaxed by the formation of misfit dislocations and stacking faults [see arrows in Fig. 2 (b)]; (ii) bright-field images taken along <110> suggest that the wetting layer is thicker than the normal wetting layer of pure Ge (3 - 5 monolayers). If this is the case it suggests that alloying might occur in the wetting layer, in agreement with Auger electron spectroscopic measurements [19].High-resolution experiments are being conducted to investigate this point; (iii) for all the islands in this study (including those which are partially relaxed), trenches were always seen around the islands, with similar dimension and cross-section profile and with a depth of approximately 7 nm (i.e. the cross-section profile and size of the trench is approximately independent of the island's size in both samples); and (iv) the island/substrate interface is about 7 nm below the flat wetting layer surface, and is at the same depth as the wetting layer/substrate interface at the bottom of the trench.

It is of interest to investigate where the Si that previously existed in the trench areas has gone. A possible process is that the Si has been transported into the islands. To test this hypothesis, cross-section TEM specimens were prepared by ion-beam thinning. To reduce the possibility of Si being sputtered onto the islands from the substrate during the cross-section specimen preparation, a copper support material was glued face-to-face to the sample surface (touching the islands), and the Ar^+ ion-beam bombarded the specimen from the copper side. These specimens were studied using an energy filtering TEM [20] which gives images mapping Si and Ge separately. Images were formed with the energy loss window centered at the Si K edge of 1839 eV and at the Ge L_3 edge of 1217 eV and with a window width of 50 eV. Examples are shown in Fig. 3. Figure 3 (a) is an image using electrons with zero energy loss showing a complete image of an island on the substrate surface covered by an epoxy resin. Figure 3 (b) is a Si map; it clearly shows the presence of Si in the island. Figure 3 (c) is a Ge map that shows the Ge island together with the thin Ge wetting layer. Note that the wetting layer appears across the entire substrate surface. Because of the strength of the Si signal from the island, and its absence from the surrounding material (epoxy), we conclude that there is Si within the dot.

If the total amount of the Si lost beneath and surrounding the island is assumed to transport to the island, the amount of Si in the island can be evaluated. As mentioned earlier, the cross-section profiles of the trenches are approximately the same (i.e. have the same dimension and shape) for all the islands studied here regardless the island sizes. Hence, we can compare the mass ratios within the islands at different growth stages. If we assume that the shape of the island is independent of size, then the mean Si composition within an island decreases with increase in size of the island. This is because the volume of the island scales as d^3 and the volume of the consumed Si substrate scales as d^2, where d represents the base diameter of the island.

Taking the above experimental observations into account, a modified S-K mode for high temperature growth of Ge islands on Si is proposed, as shown diagrammatically in Fig. 4. In classical S-K growth, layer-by-layer growth takes place at the initial stage of Ge deposition, as shown in Fig. 4 (a). However, the layer by layer growth at high temperature is accompanied by an alloying process, which results in Si transport to the wetting layer. The layer-by-layer growth is followed by island growth, as shown in Fig. 4 (b). The formation of such a small coherent island only partially releases the misfit strain. With the growth of the island, misfit strain builds up. The strain energy can be reduced in four ways: (i) by increasing the height to base diameter aspect ratios of the islands [7,21,22]; (ii) by the introduction of misfit dislocations at the interface. This requires high strain and occurs only for the larger islands; (iii) by lowering the misfit between the island and the substrate which could result from the alloying of Si into the Ge island; and (iv) by reorienting the interface to accomplish partial detachment of the island, thereby lowering the strain energy. It is evident that removal of Si from trenches of the form seen in Fig. 2 (c) and (d) will achieve strain energy reduction by mechanisms (iii) and (iv). A possible alternative mechanism to achieve mechanism (iii) [but not mechanism (iv)] would be the vertical migration of Si into the island from the region under the island. However, because surface migration [23] has a smaller activation energy than bulk migration, this alternative is less favoured. The mechanism proposed above results in a trench around the island, as illustrated in Fig. 4 (c). The subsequent island expansion necessarily starts from the bottom of the trenches and the lateral Si migration process continues as the island grows, as shown in Fig. 4 (d).

According to this model, the island/substrate interface at the centre of the island should be at a higher level (i.e. at the level of the original substrate surface) than the level of the surrounding interface. This effect has not been seen from cross-section TEM experiments. There are two possible reasons: (i) the convex interface disappears with the further growth of the islands, due to interdiffusion from the surrounding area to reduce the interface energy (the interface area reduces if the interface becomes flat), or (ii) the central interface exists, but has not yet been observed because it is too small.

As mentioned earlier, the observed trenches have approximately the same width and depth regardless of island size and strain relaxation status. This indicates that, for a given growth temperature, the migration coefficient of Si plays a crucial role in determining the trench profile. The fact that larger dots (which have larger strain) have the same size trenches as smaller dots suggests that Si migration from greater distances is limited by kinetics.

It is noted that trenches surrounding Ge islands grown on Si substrates have been reported previously. Using AFM, Kamins et al [24] found trenches surrounding Ge islands in a sample grown on Si (001) by chemical vapor deposition at a growth temperatures of 600°C. They reported that the trenches were approximately 1 nm beneath the surface, which is much shallower than the trench depths reported here. This difference can be explained by the dependence of the migration coefficient of Si on the growth temperature. This argument is further supported by the fact that Ge islands had no trench when the growth temperature was only 500°C [2]. On the other hand, Floro et al.[25] reported observation of trenches around islands in the (001) $Ge_{0.2}Si_{0.8}/Si$ sample grown by MBE at 755°C. However, the island/substrate interface in their sample is located at the original Si substrate surface. This implies that in their system the trenches might be formed only after the island growth, and can be explained by the fact that, in the case of small lattice mismatch (only about 0.8% in $Ge_{0.2}Si_{0.8}/Si$ system), the driving force for mass transportation will be smaller. Furthermore, the trenches are formed by consuming the wetting layer in the $Ge_{0.2}Si_{0.8}$ system, resulting in an uneven wetting layer thickness which is different from our observation in the Ge/Si system. The appearance of the trenches modifies the substrate surface and hence reduces the local volume of material experiencing a stress concentration.[25]

Daruka et al. [26] have investigated theoretically equilibrium phase diagrams of strained heteroepitaxial systems as a function of the coverage of deposited material and lattice mismatch for different surface energies. They have predicted seven possible phases in terms of the growth mode. However, their theory incorporated only the growth of the wetting layer, dislocation-free island formation, and ripening. Our discovery of the mass transport and alloying during the strained heteroepitaxial growth implies the existence of an extra phase due to alloying effects.

In conclusion, mass transport of Si from the Si substrate to Ge islands, and consequently alloying in the islands, has been found in the Ge/Si system grown by MBE at the temperature of 700°C. This finding suggests a modified S-K growth mode. Reduction of the misfit strain between the substrate and the islands is believed to be the driving force for the process. Besides three dimensional island growth and the formation of misfit dislocations at the interface, alloying is another way to release the misfit strain. However, since the mass transport is kinetically limited by the surface migration coefficient, alloying can only be observed at sufficiently high growth temperatures.

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Figure captions

Figure 1 Plan-view [001] on-zone bright-field images of (a) sample A and (b) sample B.

Figure 2 Cross-section bright-field images: (a) a coherent island in sample A; (b) a relaxed island in sample B where misfit dislocations at the island/substrate interface and a stacking fault are arrowed; (c) an enlarged image of a part of (a) showing a clear wetting layer. A white arrow at the left side of the image marks the interface between the wetting layer and the Si substrate. A white line below the wetting layer represents the depth level of island/substrate interface. A trench with a depth of about 7 nm at the edge of the island is clearly seen; (d) an enlarged image of a part of (b) where a trench with a similar feature to the trench in Fig. 2 (c) is clearly seen.

Figure 3 Cross-section energy filtered images: (a) a zero-loss image showing the complete morphology of the TEM specimen; (b) an energy-loss (1839 eV) image that represents a Si map. Si is clearly seen within the island; and (c) an energy-loss (1217 eV) image that represents a Ge map. A wetting layer is seen uniformly throughout the entire substrate surface.

Figure 4 Schematic diagrams of a modified S-K growth mode at different growth stages.

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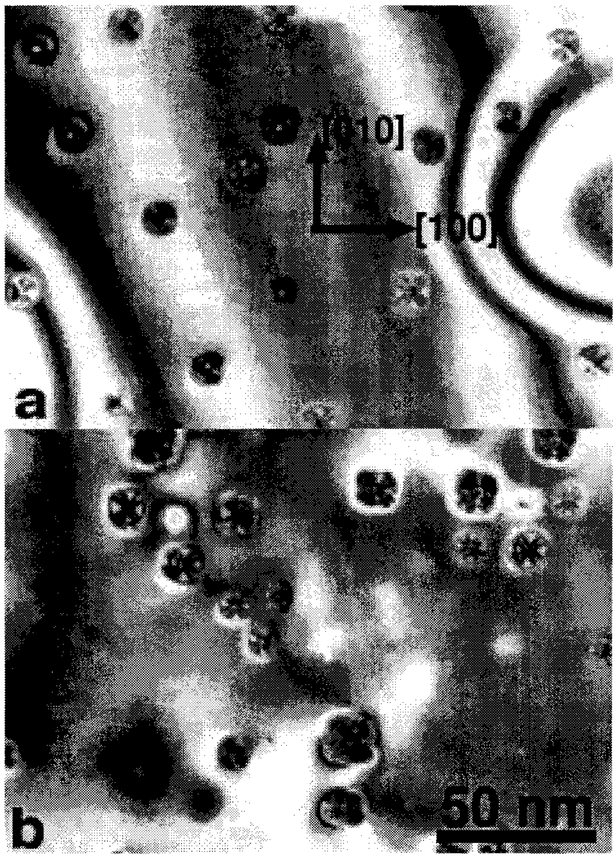
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a
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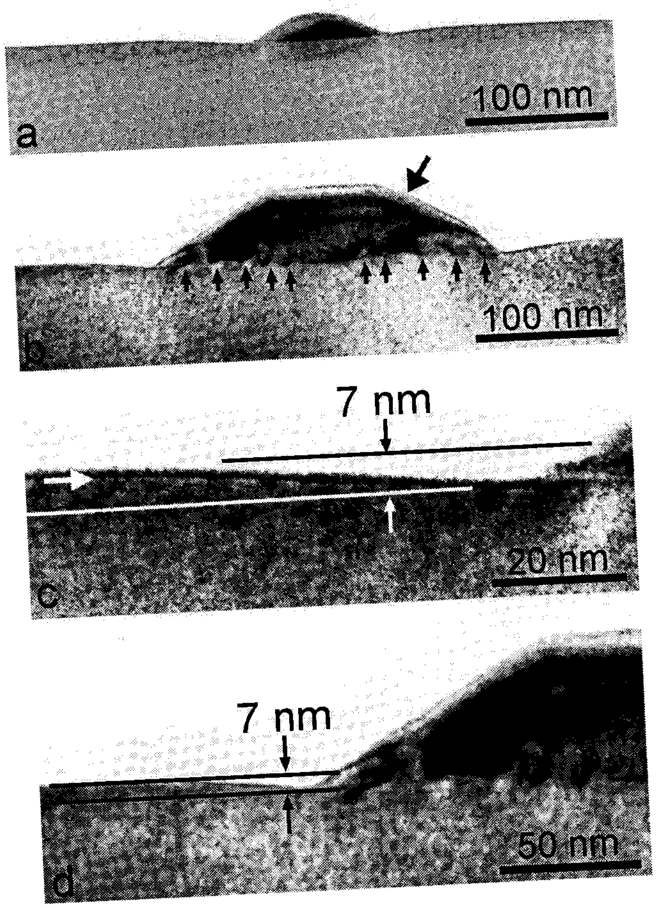
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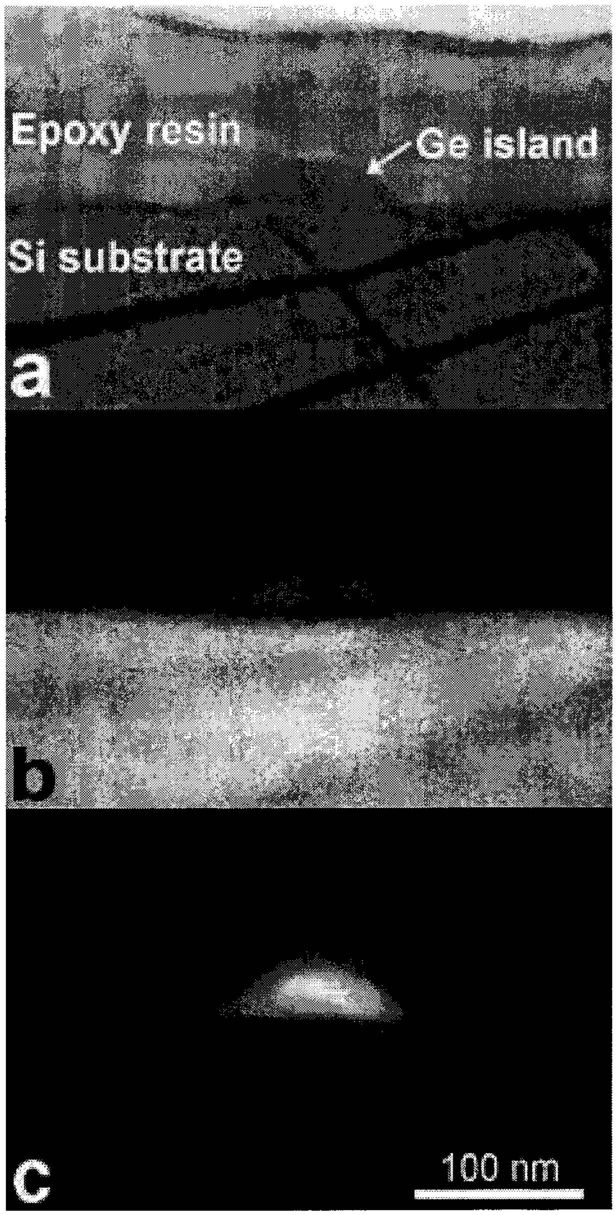

Epoxy resin
Ge island
Si substrate
a
b
c
100 nm